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Reactions of V_2O_5, Nb_2O_5, and Ta_2O_5 with AlN

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Abstract—Reactions of vanadium, niobium, and tantalum pentoxides with aluminum nitride have been studied using X-ray diffraction. At temperatures from 1000 to 1600°C, we have identified various V, Nb, and Ta nitrides. The composition of the niobium and tantalum nitrides depends on the reaction temperature. The tendency toward nitride formation becomes stronger in the order $V_2O_5 < Ta_2O_5 < Nb_2O_5$.

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INTRODUCTION

Data on reactions between refractory rare-metal oxides and aluminum nitride may be of scientific and technological interest. It is worth noting that aluminum nitride can be used as a nitriding agent in the preparation of nitrided vanadium–aluminum alloys via aluminothermic smelting. A literature search revealed no data on phase transformations in systems formed by refractory rare-metal oxides and aluminum nitride. V, Nb, and Ta are known to form stable nitrides. In particular, the Ta–N system contains two stable nitrides: Ta_2N and TaN. The stable nitrides in the Nb–N system are NbN, Nb_2N, and Nb_3N, and those in the V–N system are VN and $V_{2.15}N$.

In this paper, we present our findings on the reactions in mixtures of vanadium, niobium, and tantalum pentoxides with aluminum nitride.

EXPERIMENTAL

Phase relations in the M_2O_5–AlN systems were first modeled using detailed thermodynamic analysis [3] with the HSC-6.1 software [4]. The starting mixture composition was taken to correspond to the reaction stoichiometry

$$3M_2O_5 + 10AlN = 6MN + 5Al_2O_3 + 2N_2, \qquad (1)$$

which was selected based on preliminary analysis of phase equilibria at AlN : M_2O_5 weight ratios from 0 to 3 and temperatures below 1500°C. The possible reaction products included elemental metals, their nitrides (VN, NbN, Nb_2N, $NbN_{0.88}$, Nb_3N, TaN, Ta_2N) and aluminides (VAl_3, V_5Al_8, V_2Al_3, $NbAl_3$, Nb_2Al, Nb_3Al), and condensed and gaseous metal oxides and nitrogen oxides (NO, NO_2) represented in the HSC-6.1 database. The amount of the inert gas (helium) was 0.1 kmol.

Phase transformations were explored by X-ray diffraction (XRD) of reaction products obtained by heating compacted mixtures of the Group V-B metal pentoxides and aluminum nitride in an inert atmosphere. The starting mixtures were prepared by a conventional ceramic processing technique and were compacted at a pressure of 10 MPa. The compacts were fired in a helium-filled SShVL-0,6.2/16I2 furnace. The heating rate was 7–10°C/min, and the isothermal hold time was 0.5–1 h. The starting materials used were analytical-grade vanadium pentoxide, pure-grade niobium and tantalum pentoxides, and SVS TCh-1 aluminum nitride (produced at the Institute of Structural Macrokinetics and Materials Science, Russian Academy of Sciences, Chernogolovka, Russia).

RESULTS AND DISCUSSION

Figure 1 illustrates the modeling results for reactions of vanadium, niobium, and tantalum pentoxides with AlN. Below 1000°C, the condensed metallic product of the reaction between V_2O_5 and aluminum nitride consists only of VN. Above this temperature, less AlN is involved in the reduction of vanadium. For $t > 1250°C$, elemental vanadium is likely to form together with VN. For $t > 2000°C$, the likely reaction products are V_3Al_2 and elemental aluminum. Near 2500°C, the VN content may drop to 26 wt % and the vanadium, aluminum, and V_3Al_2 contents may increase to 53.0, 3.0, and 12.0 wt %, respectively.

Therefore, according to the thermodynamic modeling results, during heating of a stoichiometric $3V_2O_5 + 10AlN$ mixture the degree of vanadium nitriding should decrease monotonically from 57.0% for $t \leq 1000°C$ to 9.5% at 2500°C. Al_2O, AlO, and VO vaporization is insignificant. The equilibrium NO and NO_2 concentrations in the gas phase do not exceed 10^{-3}% up to 2500°C. The oxide product consists

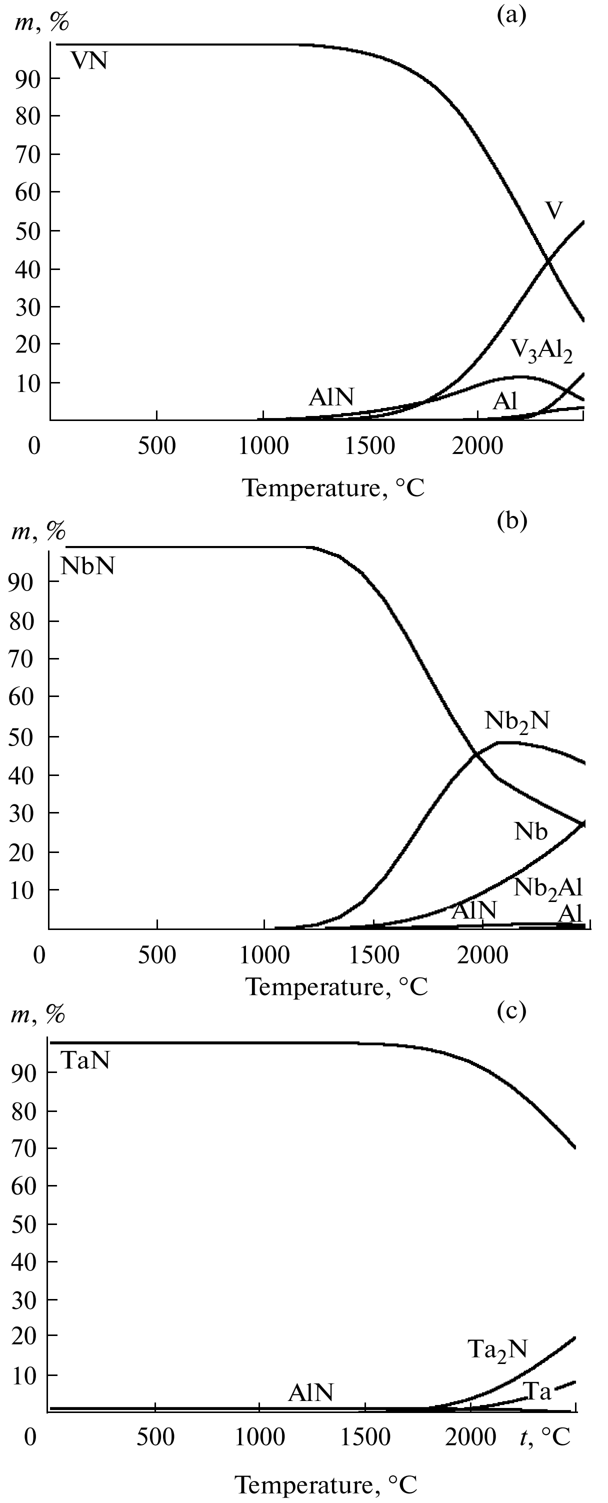

Fig. 1. Temperature effect on the equilibrium composition of the metallic phase for reactions of AlN with (a) vanadium, (b) niobium, and (c) tantalum.

largely of Al_2O_3 up to 1000°C. The VO + V_2O_3 content in this temperature range is below 1.0%. With increasing temperature, the equilibrium concentration of V_2O_3 decreases and that of VO increases. The VO concentration increases most markedly above 1000°C. At high temperatures, e.g., at 1500 and 2500°C, the equilibrium VO concentration is 5.0 and 33.0%, respectively. The contents of the other vanadium oxides, VO_2 and V_3O_5, are insignificant, within 0.2% at 2500°C. In addition, the equilibrium AlN content increases markedly at high temperatures, with a maximum (12.0%) at 2200°C. For $t > 2000$°C, the metallic phase contains elemental aluminum. Its content reaches 3.5% at 2500°C.

The metallic products of the reaction between Nb_2O_5 and aluminum nitride are NbN, Nb_2N, and elemental niobium. At temperatures below 1200°C, the NbN content may exceed 99.0 wt %. In the temperature range 1200–2080°C, the equilibrium concentration of NbN decreases and those of elemental niobium and Nb_2N increase. The Nb_2N content has a maximum (48.0%) at 2080°C and drops to 43.0% at 2500°C. The elemental niobium content increases steadily, reaching 28.0% at 2500°C. This variation in the relationship between the equilibrium phases seems to be caused by Nb_2N decomposition above 2100°C [1, 2]. In the temperature range 1500–2500°C, aluminum nitride and elemental aluminum are present in significant concentrations.

The fraction of nitrogen from AlN consumed in niobium nitriding by reaction (1) decreases from 60% for $t \leq 1000$°C to 25.0% at 2500°C. At temperatures below 2000°C, the vapor phase contains insignificant amounts of aluminum and niobium suboxides and nitrogen oxides.

Condensed NbO_2 and NbO may be formed over the entire temperature range examined. The predominant oxide is NbO_2 below 1300°C and NbO at higher temperatures. The percentage of NbO rises monotonically and reaches a significant level above 1000°C. The oxides present at 2500°C are Al_2O_3 (77.5%), NbO (20.5%), and NbO_2 (1.75%).

When a stoichiometric $3Ta_2O_5 + 10AlN$ mixture is heated to 1500°C, reaction (1) may reach completion. Only above 1500°C may the conversion of AlN to tantalum nitrides decrease. Below 1500°C, the nitriding product is TaN. At higher temperatures, the reaction gives TaN, Ta_2N, and elemental tantalum. Significant amounts of elemental tantalum and Ta_2N may form above 2000°C.

The oxide component is Al_2O_3 (>99.9%). Only in the range 2000–2500°C may slight amounts of Ta_2O_5 and AlO be present.

Below 2000°C, the gas phase consists of only nitrogen and helium, which was present in the working medium. The content of nitrogen oxides is within 92%. Above 2000°C, tantalum and aluminum suboxides are likely to form and sublime.

The experimental data obtained during heating of $xM_2O_5 + yAlN$ mixtures are summarized in Tables 1–3. It can be seen from Table 1 that, below 1600°C, V_2O_5 and AlN react to form V_2N. The condensed phase

Table 1. Phase composition of the products of reaction between V_2O_5 and AlN

Initial AlN/V_2O_5 molar ratio	Phase composition of firing products			
	1000°C	1100°C	1200°C	1600°C
9.00	AlN, V_2O_3	AlN, AlV_2O_4, Al_2O_3	AlN, VO, Al_2O_3	AlN, VO, Al_2O_3, V_2N
7.44	AlN, V_2O_3, Al_2O_3	AlN, Al_2O_3, VO	AlN, VO, Al_2O_3	
5.66	AlN, V_2O_3	AlN, AlV_2O_4, V_2O_3, Al_2O_3	AlN, VO, Al_2O_3, AlV_2O_4, V_2N	AlN, VO, Al_2O_3, V_2N
4.00	AlN, V_2O_3	AlN, AlV_2O_4, V_2O_3, Al_2O_3	AlN, VO, Al_2O_3, V_2N	AlN, VO, Al_2O_3, V_2N
3.33	AlN, V_2O_3, VO, Al_2O_3	AlN, V_2O_3, VO, Al_2O_3	AlN, VO, Al_2O_3, V_2N	
2.33	AlN, V_2O_3	AlN, V_2O_3, AlV_2O_4, Al_2O_3	AlN, AlV_2O_4, Al_2O_3, V_2N	VO, Al_2O_3, V_2N, AlV_2O_4, V_3Al
1.22	AlN, V_3O_5, V_4O_7	AlN, V_3O_5, Al_2O_3	AlN, V_3O_5, V_2O_3, Al_2O_3, V_2N	V_2O_3–Al_2O_3 solid solution
0.67	VO_2, Al_2O_3	AlN, VO_2, Al_2O_3	VO_2, Al_2O_3, V_2N	V_2O_3–Al_2O_3 solid solution

Table 2. Phase composition of the products of reaction between Nb_2O_5 and AlN

Initial AlN/Nb_2O_5 molar ratio	Phase composition of firing products			
	1000°C	1200°C	1400°C	1600°C
0.50	Nb_2O_5, NbO_2, AlN	NbO_2, Nb_2O_5, AlN	NbO_2 solid solution	NbO_2 solid solution
1.22	Nb_2O_5, NbO_2, AlN	NbO_2, NbN, Al_2O_3	NbO_2, Nb_4N_3, Al_2O_3	NbO_2, Nb_4N_3, Al_2O_3
2.00	Nb_2O_5, NbO_2, AlN	NbO_2, NbN, $NbN_{0.95}$, Al_2O_3	NbO_2, Nb_4N_3, Al_2O_3	NbO_2, Nb_4N_3, Al_2O_3
3.33	Nb_2O_5, NbO_2, AlN	NbO_2, NbN, $NbN_{0.95}$, Al_2O_3	NbN, Al_2O_3	Nb_4N_3, Al_2O_3
5.00	Nb_2O_5, NbO_2, AlN, NbN	NbN, $NbN_{0.95}$, Al_2O_3, AlN	Nb_4N_3, $NbN_{0.95}$, Al_2O_3, AlN	Nb_4N_3, Al_2O_3, AlN
8.00	Nb_2O_5, NbO_2, AlN, NbN	NbN, $NbN_{0.95}$, Al_2O_3, AlN	NbN, Al_2O_3, AlN	Nb_4N_3, Al_2O_3, AlN

Table 3. Phase composition of the products of reaction between Ta_2O_5 and AlN

Initial composition of reaction products	*t*, °C	Phases identified
$Ta_2O_5 + 3AlN$	1000	Ta_2O_5, AlN
	1100	Ta_2O_5, AlN, $AlTaO_4$
	1200	Ta_2O_5, AlN, $AlTaO_4$
	1500	Ta_2N, Al_2O_3, TaN
$Ta_2O_5 + 5AlN$	1000	Ta_2O_5, AlN
	1100	Ta_2O_5, AlN, $AlTaO_4$
	1200	Ta_2O_5, AlN, $AlTaO_4$, Ta_5N_6
	1500	Ta_2N, Al_2O_3
$Ta_2O_5 + 8AlN$	1000	Ta_2O_5, AlN
	1100	Ta_2O_5, AlN, $AlTaO_4$
	1200	Ta_2O_5, AlN, $AlTaO_4$, Ta_5N_6
	1500	Ta_2N, Al_2O_3

consists of vanadium and aluminum oxides. The starting mixture composition and temperature have a systematic effect on the phase composition of the products of V_2O_5 reduction with aluminum nitride. For example, it can be seen from Table 1 and Fig. 2 that increasing the AlN/V_2O_5 ratio in the starting mixture from 0.67 to 9.0 changes the valence state of vanadium as follows: from VO_2 to V_2O_3 at $t = 1000°C$, from VO_2 to VO at 1200°C, and from V_2O_3 to VO at 1600°C. V_2N formation begins at $t \geq 1200°C$. At $t \geq 1600°C$, the vanadium aluminide V_3Al may form. According to Elyutin and Pavlov [5], the reaction of V_2O_5 with AlN follows Baikov's principle of transformation sequence:

$$V_2O_5 \rightarrow VO_2 \rightarrow V_4O_7$$
$$\rightarrow V_3O_5 \rightarrow V_2O_3 \rightarrow VO \rightarrow V_3Al.$$

Chemical analysis for nitrogen in the products of the reaction of AlN with V_2O_5 and thermogravimetric data indicate that, in addition to the reactions

$$3V_2O_5 + 2AlN = 6VO_2 + Al_2O_3 + N_2, \qquad (2)$$

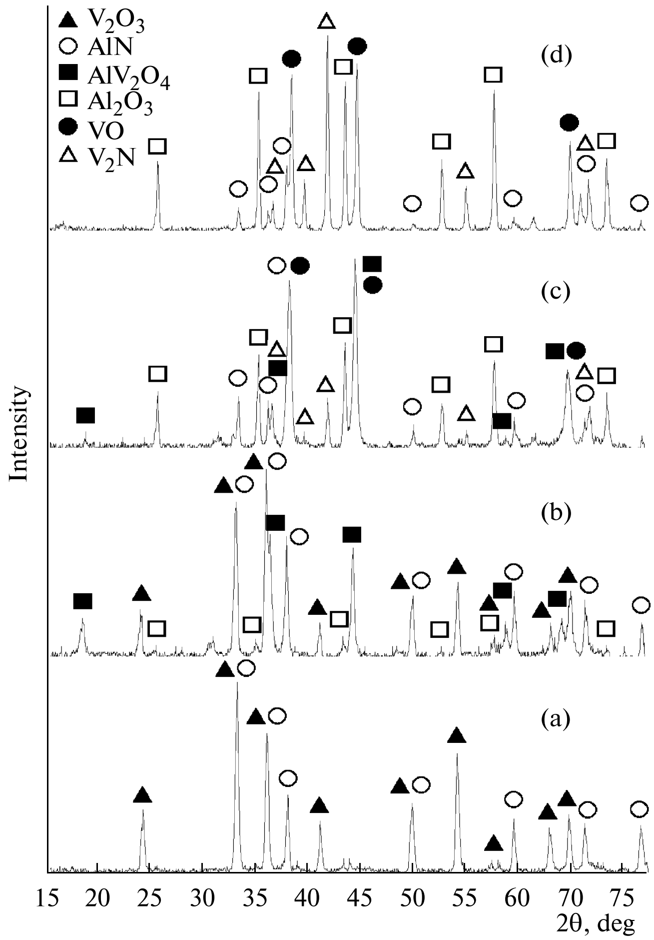

Fig. 2. XRD patterns of the products of reaction between V_2O_5 and AlN at $AlN/V_2O_5 = 4.00$ and temperatures of (a) 1000, (b) 1100, (c) 1200, and (d) 1600°C.

$$4VO_2 + 2AlN = V_2O_3 + 2VO + Al_2O_3 + N_2, \qquad (3)$$

$$3V_2O_3 + 2AlN = 6VO + Al_2O_3 + N_2, \qquad (4)$$

$$6VO + 4AlN = 3V_2N + 2Al_2O_3 + 0.5N_2, \qquad (5)$$

$$3VO + 3AlN = V_3Al + Al_2O_3 + 1.5N_2, \qquad (6)$$

with $\Delta G_{(2)} = -640826 - 206.95T$ (298–998 K), $\Delta G_{(2)} = -378451 - 259.38T$ (1798–2773 K), $\Delta G_{(3)} = -286228 - 115.36T$ (298–1798 K), $\Delta G_{(3)} = -209099 - 130.01T$ (2198–2773 K), $\Delta G_{(4)} = 39893 - 159.91T$ (298–1998 K), and $\Delta G_{(4)} = 124345 - 216.33T$ (2198–2773 K), the lower vanadium oxides react with AlN at high temperatures, which may be accompanied by the formation and release of nitrogen oxides, e.g., by the reaction

$$5VO_2 + 2AlN = 5VO + Al_2O_3 + 2NO. \qquad (7)$$

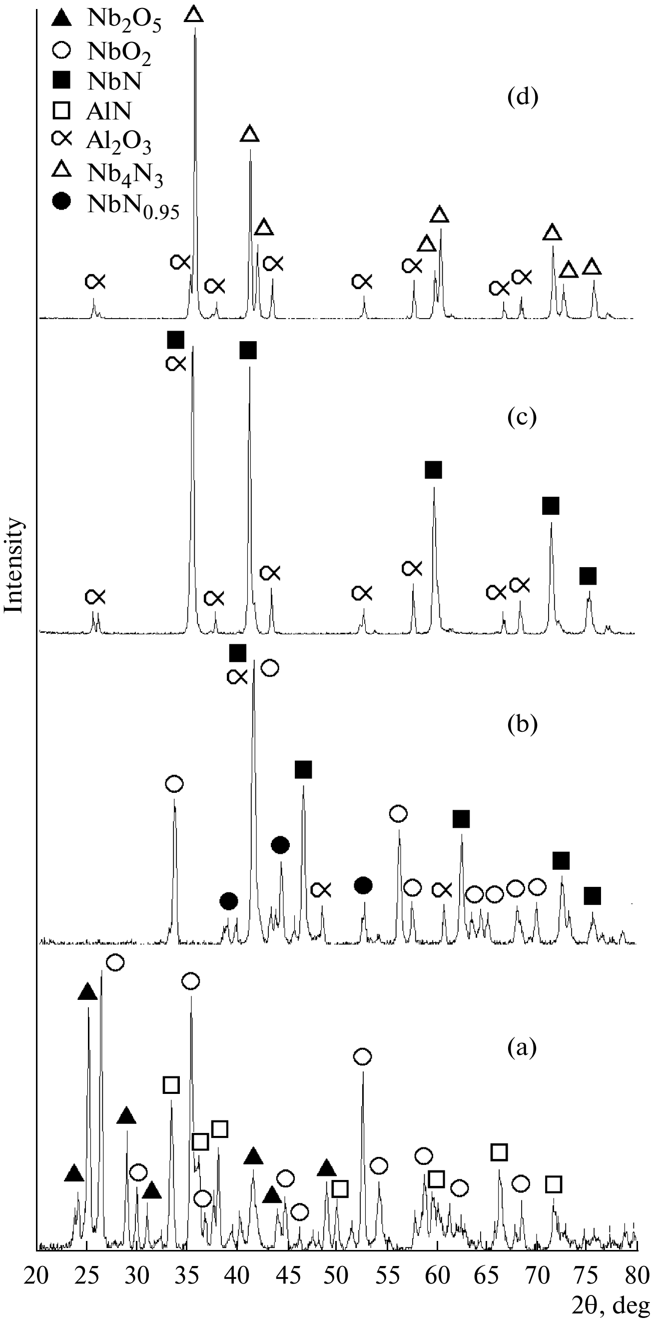

Fig. 3. XRD patterns of the products of reaction between Nb_2O_5 and AlN at $AlN/Nb_2O_5 = 3.33$ and temperatures of (a) 1000, (b) 1100, (c) 1200, and (d) 1600°C.

The XRD results for the products obtained by heating mixtures with different AlN/Nb_2O_5 ratios demonstrate that the primary product of the reaction between aluminum nitride and Nb_2O_5 is niobium dioxide (Table 2, Fig. 3). At temperatures above 1200°C and $AlN/Nb_2O_5 \le 1.2$, the forming niobium dioxide dissolves the starting niobium pentoxide. Niobium dioxide (or a NbO_2–Nb_2O_5 solid solution) was identified in the products obtained by heating mixtures substoichiometric for reaction (1) to 1600°C. Heating mixtures with $AlN/Nb_2O_5 \geq 3.33$ led to niobium dioxide formation at temperatures below 1200°C.

NbN formation begins in mixtures close in stoichiometry to the reaction

$$Nb_2O_5 + 1.2AlN = 1.6NbO_2 + 0.6Al_2O_3 + 0.4NbN + 0.4N_2, \quad (8)$$

with $\Delta G_{(8)} = -86068 - 51.25T$ (298–1898 K) and $\Delta G_{(8)} = 21063 - 90.828T$ (2198–2773 K).

No niobium dioxide was detected in the reaction products obtained above 1200°C in mixtures with AlN/Nb_2O_5 ratios equal to or greater than the stoichiometric ratio for the reaction

$$Nb_2O_5 + \frac{10}{3}AlN = 2NbN + \frac{5}{3}Al_2O_3 + \frac{2}{3}N_2, \quad (9)$$

with $\Delta G_{(9)} = -305605 - 72.727T$ (298–1898 K) and $\Delta G_{(9)} = -136554 - 134.4T$ (2298–2773 K).

At higher temperatures, niobium dioxide is reduced to NbN and Nb_2N by the reactions

$$3NbO_2 + 4AlN = 3NbN + 2Al_2O_3 + 0.5N_2, \quad (10)$$

$$3NbO_2 + 4AlN = 1.5Nb_2N + 2Al_2O_3 + 1.75N_2, \quad (11)$$

with $\Delta G_{(10)} = -410812 - 38.852T$ (298–2198 K), $\Delta G_{(10)} = -287879 - 83.296T$ (2398–2773 K); $\Delta G_{(11)} = -85207 - 184.47T$ (298–2198 K), $\Delta G_{(11)} = -147879 - 145.21T$ (2398–2773 K).

Nb_4N_3 may result from the reaction

$$2NbN + Nb_2N \longrightarrow Nb_4N_3. \quad (12)$$

Nb_4N_3 formation by this reaction is evidenced by the temperature effect on the phase composition of the reaction products, especially for the mixtures with $AlN/Nb_2O_5 \geq 3.33$. In the temperature range 1200–1400°C, the strongest reflections in the XRD patterns of the products of the reaction between AlN and Nb_2O_5 in such mixtures are those from $NbN_{0.95}$ because of the high rate of reactions (9) and (10).

In the Ta_2O_5–AlN system, we studied mixtures indicated in Table 3. Our results demonstrate that the reaction between aluminum nitride and Ta_2O_5 begins above 1000°C and gives a phase identified as $AlTaO_4$. This double oxide is probably a reaction intermediate. XRD results (Fig. 4) demonstrate that, with increasing temperature, the $AlTaO_4$ content first increases and then drops. At 1500°C, the XRD peaks of $AlTaO_4$ are indiscernible from the background level.

The XRD patterns of the mixtures heated to 1200°C showed reflections from TaN and Ta_5N_6. At 1500°C, the major phase was Ta_2N, which was probably formed by the reactions

$$3Ta_2O_5 + 10AlN = 3Ta_2N + 5Al_2O_3 + 3.5N_2, \quad (13)$$

with $\Delta G_{(13)} = 102509 - 518.22T$ (298–2773 K), and

$$6AlTaO_4 + 10AlN = 3Ta_2N + 8Al_2O_3 + 3.5N_2. \quad (14)$$

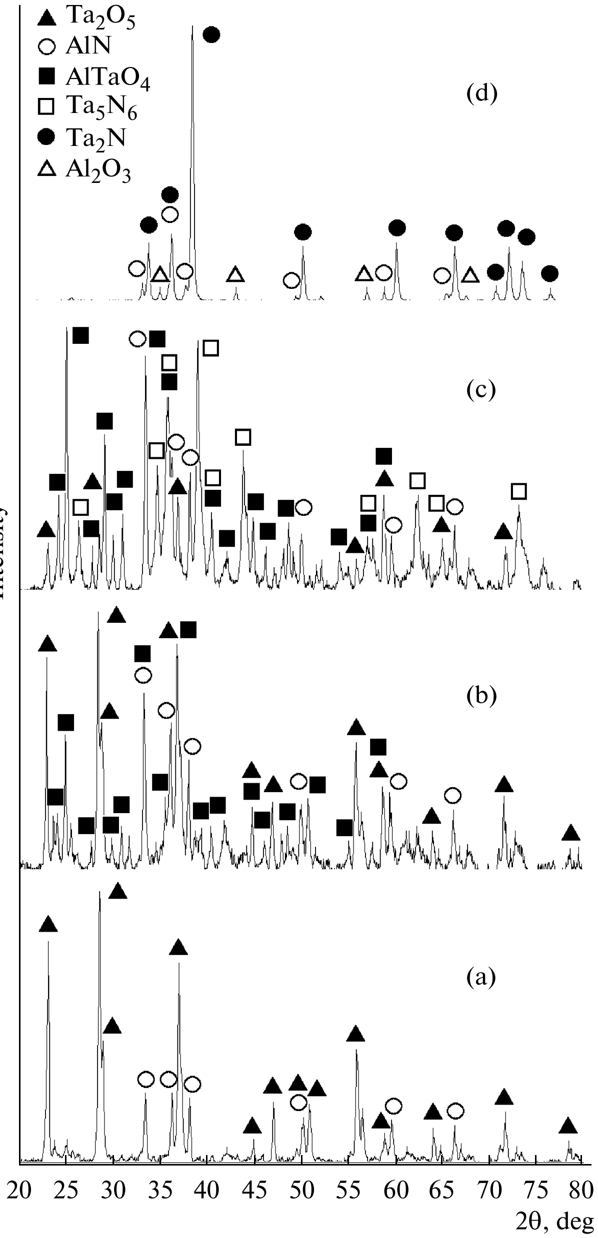

Fig. 4. XRD patterns of the products of reaction between Ta_2O_5 and AlN at $AlN/Ta_2O_5 = 5$ and temperatures of (a) 1000, (b) 1100, (c) 1200, and (d) 1500°C.

Characteristically, the TaN and Ta_5N_6 contents are independent of the firing temperature and initial AlN content. After heating the mixtures with $AlN/Ta_2O_5 > 3.33$ to 1500°C, no excess aluminum nitride was detected by XRD. One possible reason for this is that AlN dissolved in the tantalum nitride.

CONCLUSIONS

The following nitrides were identified by XRD in the products of reactions between the Group V-B metal pentoxides and AlN: V_2N, NbN, $NbN_{0.95}$, Nb_4N_3, Ta_5N_6, TaN, and Ta_2N. The composition of the niobium and tantalum nitrides depends on the reaction temperature. The tendency toward nitride formation becomes stronger in the order $V_2O_5 < Nb_2O_5 < Ta_2O_5$.

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